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UNPUBLISHED PRELIMINARY DATA

FUNDAMENTAL STUDIES OF THE METALLURGICAL,
ELECTRICAL, AND OPTICAL PROPERTIES OF
GALLIUM PHOSPHIDE

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LEWIS RESEARCH CENTER
CLEVELAND, OHIO

Work Performed By

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Stanford, California

PROJECT 5005:   BAND STRUCTURE OF GALLIUM PHOSPHIDE

The objective of this project is the experimental determination of the electronic band structure of gallium phosphide over a wide range of temperature.

The investigation of the band structure of this material will consist of three areas of effort: 1) the measurement of the optical absorption in the region of the band edge, 2) the measurement of the optical reflectivity of the material in the vacuum ultraviolet, and 3) the measurement of photoemission from the material in this same range of photon energy. The second and third portions of this effort are just being begun with the construction of a chamber for reflectivity measurements and a preliminary photoemission tube now in progress. The first area is essentially completed and is described herein.

A.   OPTICAL ABSORPTION OF GALLIUM PHOSPHIDE NEAR THE ABSORPTION EDGE

In this report, the theory of the optical absorption of an indirect semiconductor near the band edge is reviewed for a comparison with

experimental results. Equipment is described for the measurement of the transmission of crystals at temperatures up to 900 °K and the results of preliminary measurements made on a gallium phosphide crystal are presented. The band gap is found to vary as a function of temperature as $E_g = 2.312 - 4.2 \times 10^{-4}\, T$ electron volts where T is in degrees Kelvin. The energy of the phonon (or combination of phonons) involved in the transition is found to be about 0.034 ev for temperatures in the 200 °K to 600 °K range.

B. THEORY

The theoretical analysis of the optical properties of indirect semiconductors has been carried out by a number of workers [Ref. 1]. In a photon-induced transition between a valence band maximum at k = 0 and a conduction band minimum at $k_m \neq 0$, a phonon (or phonons) must be emitted or absorbed in the process in order to conserve momentum. Since the probability of the process going with the absorption of a phonon is proportional to the number of phonons present, N_s, and the probability of phonon emission is proportional to $N_s + 1$, the absorption coefficient for the material near the band edge should vary as

$$\alpha h\nu = \text{const} \left[N_s (h\nu - E_g + E_{ph})^2 + (N_s + 1)(h\nu - E_g - E_{ph})^2 \right] \quad (1)$$

where $h\nu$ is the photon energy, α the absorption coefficient, E_g the energy gap, and E_{ph} the energy of the assisting phonon.

The number of phonons of energy E_{ph} is given by

$$N_s = N \frac{1}{e^{E_{ph}/kT} - 1} \quad (2)$$

which substituted into Eq. (1) gives

$$\alpha h\nu = \text{const} \left[\frac{(h\nu - E_g + E_{ph})^2}{e^{E_{ph}/kT} - 1} + \frac{(h\nu - E_g - E_{ph})^2}{1 - e^{-E_{ph}/kT}} \right] \quad (3)$$

1Smith, Semiconductors, Cambridge Press, London, pp. 201-210.

Expanding (3) and writing it in terms of the hyperbolic cotangent we have

$$\alpha h\nu = \text{const} \left\{ (h\nu - E_g)^2 \coth \frac{E_{ph}}{2kT} - 2(h\nu - E_g) E_{ph} + E_{ph}^2 \coth \frac{E_{ph}}{2kT} \right\} .$$

(4)

Since

$$\coth \frac{E_{ph}}{2kT} \left(h\nu - E_g - E_{ph} \tanh \frac{E_{ph}}{2kT} \right)^2$$

$$= (h\nu - E_g)^2 \coth \frac{E_{ph}}{2kT} - 2(h\nu - E_g) E_{ph} + E_{ph}^2 \tanh \frac{E_{ph}}{2kT} ,$$

(5)

we may approximate (4) by (5) in the higher absorption region where $(h\nu - E_g)^2 \coth \frac{E_{ph}}{2kT} \gg E_{ph}^2 \left(\coth \frac{E_{ph}}{2kT} - \tanh \frac{E_{ph}}{2kT} \right)$. Hence for $h\nu$ somewhat greater than $E_g + E_{ph}$ we have

$$\alpha h\nu = A \left(\coth \frac{E_{ph}}{2kT} \right) \left(h\nu - E_g - E_{ph} \tanh \frac{E_{ph}}{2kT} \right)^2 \quad \text{for} \quad h\nu > E_g + E_{ph} .$$

(6)

For photon energies between $E_g - E_{ph}$ and $E_g + E_{ph}$ the second term in Eq. (1) and Eq. (3) is zero and we have

$$\alpha h\nu = A \frac{(h\nu - E_g + E_{ph})^2}{e^{E_{ph}/kT} - 1} \quad \text{for} \quad E_g - E_{ph} < h\nu < E_g + E_{ph}$$

(7)

where A is the same constant as in (6). For photon energies below $E_g - E_{ph}$, the absorption should be zero

From Eq. (6) and Eq. (7), we see a plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ should consist of two straight line segments as shown in Fig. 66. If both segments of this curve are experimentally observed at a single temperature then the value of the energy gap and assisting phonon energies may be calculated from the intercepts with the $\alpha h\nu = 0$ axis. If only the higher absorption segment of the curve is experimentally observed, then
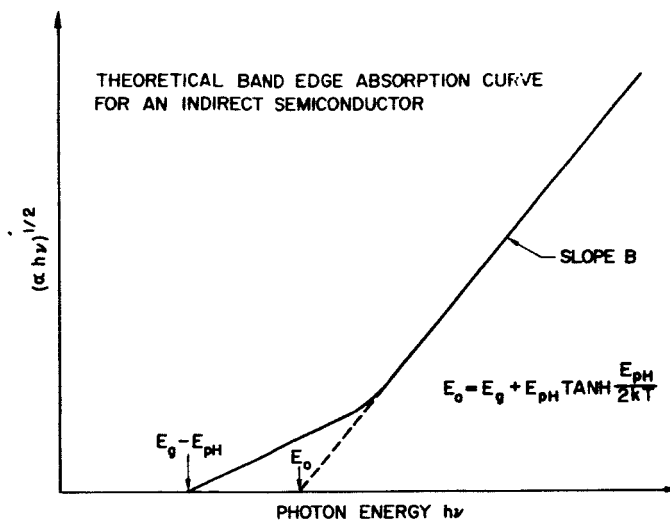
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FIG. 66. THEORETICAL $(\alpha h\nu)^{1/2}$ vs $h\nu$ CURVE.

E_g and E_{ph} may still be obtained if measurements are carried out over a range of temperatures. The method of doing this is to observe that the slope of the $(\alpha h\nu)^{1/2}$ curve should be proportional to $(\coth E_{ph}/2kT)^{1/2}$ and hence the value of E_{ph} is selected which best fits the measured slope vs temperature relation. Knowing the value of E_{ph}, one may calculate the value of E_g as a function of temperature from the intercept of the curve.

C. MEASUREMENT EQUIPMENT

The experimental measurements were carried out on gallium phosphide, a semiconductor of special interest for its possible use at high temperatures. Because of this possible high temperature applicability, it was decided to study the material over a temperature range of from $-50\ ^\circ C$ up to $600\ ^\circ C$. In order to carry out useful measurements for the determination of E_{ph} and E_g, as described previously, good optical equipment combined with close temperature control of the sample is essential. In addition, for the higher temperatures the sample must be protected from deterioration by oxidation, etc.

In order to satisfy these measurement requirements, a vacuum dewar with a temperature-feedback-controlled sample heater was constructed for use in the Cary Model 14 recording spectrophotometer. The center tube

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of the dewar is filled with liquid nitrogen to act as a coolant for below-room temperature measurements and as a "cold finger" to maintain a better vacuum. The gallium phosphide disc is mounted in a steel tube (for a constant-temperature environment) which is loosely thermally coupled to the cold finger. Two thermocouples are mounted near the sample in the tube; one is used to monitor the sample temperature and the other to provide the temperature feedback for the temperature-control mechanism. The heater is wrapped around the outside of the sample tube and is driven by a transistor amplifier. The feedback control mechanism provides a stable sample temperature which may be easily kept within a degree of any desired temperature.

D. EXPERIMENTAL RESULTS

The output of the spectrophotometer obtained at a given temperature is a graph of optical density vs wavelength, where the optical density is defined as

$$\text{optical density} = \log_{10}\left(\frac{\text{Incident Intensity}}{\text{Transmitted Intensity}}\right). \qquad (8)$$

The transmitted intensity will be less than the incident intensity due to surface reflections, bulk absorption as described by Eq. (6) and Eq. (7), and so-called "free carrier" absorption. Since we are interested only in the second of these contributions, we wish to compensate for the reflection and free carrier contributions. We do this by noting that below the absorption edge these are the only contributions to the sample absorption and that, ignoring multiple reflections, their contributions should remain relatively constant in the region of the band edge. Hence the optical density curve is corrected by extrapolating the below-band edge absorption to the band edge region and subtracting this value from the observed optical density to get the desired electronic contribution [Ref. 2]. The absorption coefficient, defined by $I(x) = I_o e^{-\alpha x}$ is then given by

$$\alpha = \frac{\log_e 10}{d} \text{ optical density} = \frac{2.3026}{d} \text{ optical density}, \qquad (9)$$

where d is the thickness of the sample.

[2] G. G. MacFarlane and V. Roberts, Phys. Rev., 97, 1714, ibid., 95, 1865.

The measurements were made on a gallium phosphide sample grown by the float zone technique and sulfur doped to 0.1 to 0.2 ohm-cm resistivity at room temperature. A typical $(\alpha h\nu)^{1/2}$ vs $h\nu$ curve is shown in Fig. 67 for a temperature of 400 °C. It is noted that while the points
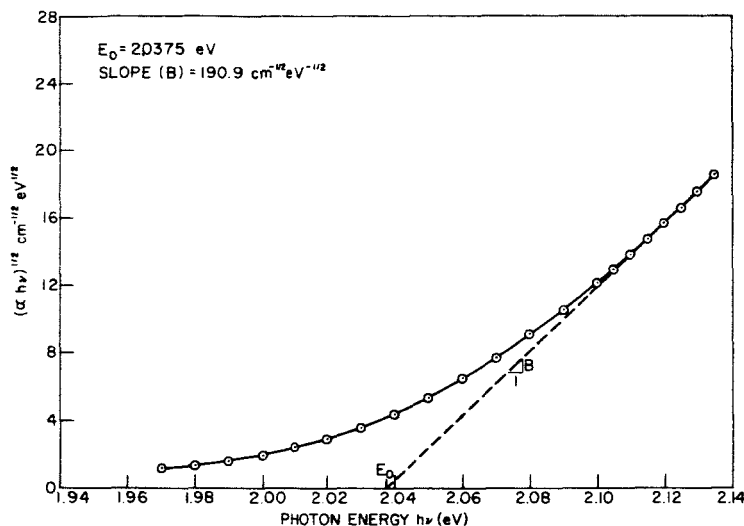

FIG. 67. $(\alpha h\nu)^{1/2}$ VS $h\nu$ FOR GaP SAMPLE AT 400 °C.

fit a nice straight line at higher values of α, on the low-energy end the curve tails off into an exponential. Figure 68 shows that for over an order of magnitude in absorption in this tail the curve fits an exponential very accurately. This $\alpha = \alpha_o e^{h\nu/s}$ type of dependence of absorption at low α is known as an "Urback tail" and is found in most of the less-pure semiconductors. The effect here is to make it impossible to see any distinct lower segment of the absorption curve and hence the second technique mentioned for evaluating E_{ph} and E_g must be used.

The absorption curves of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for various temperatures are shown in Fig. 69. The slopes of these curves (squared) are plotted in Fig. 70 together with the "best fit" $\coth E_{ph}/2kT$ curve which is obtained for $E_{ph} = 0.034$ ev. It should be noted that this value of E_{ph} fits the points accurately only up to about 400 °C whereupon the slopes fall below the expected values. The energy gap calculated using

ABSORPTION VERSUS LIGHT FREQUENCY

EXPONENTIAL TAIL REGION

GALLIUM PHOSPHIDE

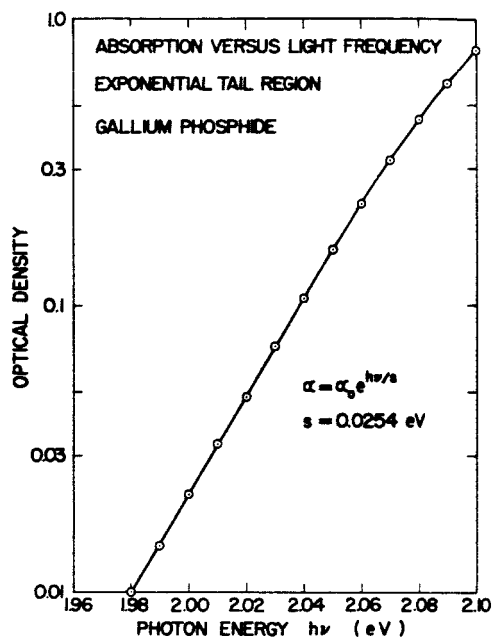$\alpha = \alpha_s e^{h\nu/s}$

$s = 0.0254$ eV

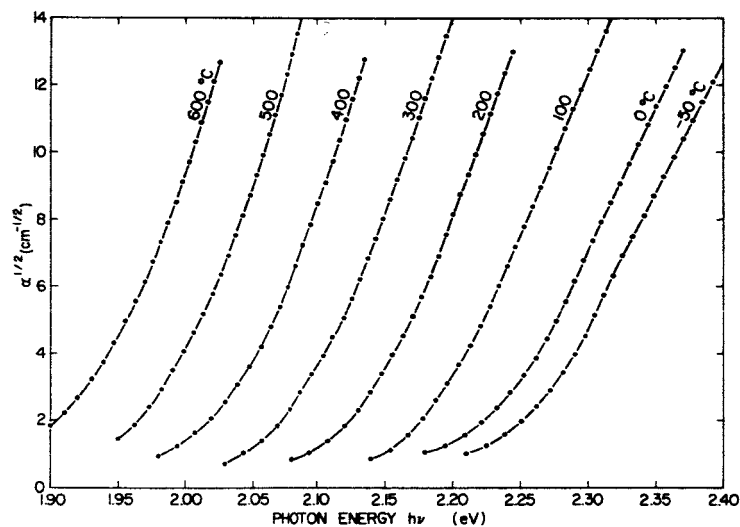FIG. 68. OPTICAL DENSITY VS $h\nu$
FOR GaP AT 400 °C.

FIG. 69. TRANSMISSION CURVES OF GaP AT
VARIOUS TEMPERATURES $\alpha^{1/2}$ VS $h\nu$.

this value of phonon energy is graphed vs temperature in Fig. 71. For temperatures up to 400 °C the energy gap relation is
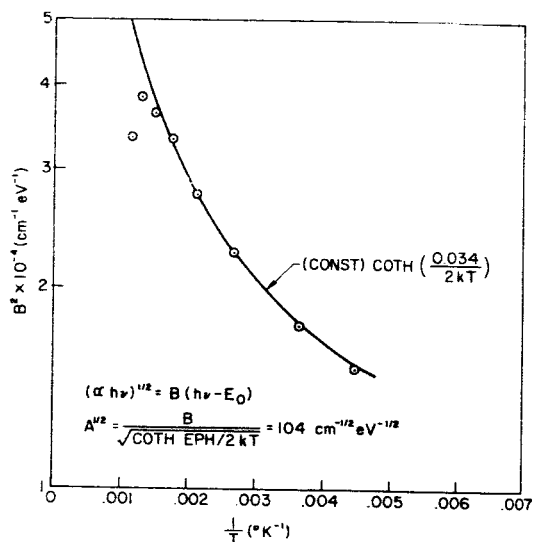
$$E_g = 2.312 - 4.2 \times 10^{-4} \ T \ ev$$

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FIG. 70. SEMILOG PLOT OF B^2 AND COTH $(0.034/2kT)$ PLOTTED VS $1/T$ DATA POINTS FOR GALLIUM PHOSPHIDE.
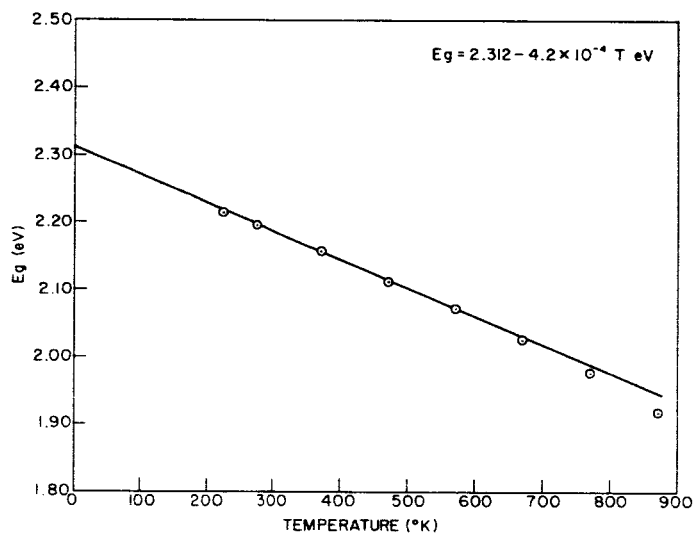

FIG. 71. ENERGY CAP VS TEMPERATURE FOR GALLIUM PHOSPHIDE.

with all points within 0.005 ev of this. At higher temperatures the energy gap drops below this curve (about 0.028 ev below at 600 °C).

E. DISCUSSION

The results of the measurements on the GaP sample agree very well with the theory, perhaps even better than one would expect considering

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the fact that the theory discussed considers only one type of assisting phonon whereas the phonon dispersion relation is actually quite complex and a number of different phonons could be involved in this transition. The fact that the slope data for temperatures between -50 °C and 400 °C can be fitted to good accuracy with a single phonon energy indicates that in this temperature range, one phonon (or combination of phonons) predominates in the transition. It is not particularly surprising that at higher temperatures (600 °C) this might change somewhat.

The only significant variation of the observed results from the theory is in the presence of the exponential tail on the absorption curve. This tail is probably due to the presence of impurities in the sample. One mechanism explaining the production of such a tail by charged impurities has been discussed by Redfield [Ref. 3]. Redfield calculates the effect on the absorption characteristic produced by high electric fields surrounding charged impurities acting on the crystal absorption through the Franz-Keldysh effect. For the case of a direct-bandgap material he finds the $\alpha(E_g)$ (the absorption coefficient at the energy gap) should vary as the nine halves power of the charged impurity density. His calculations are in good agreement with the measurements of Dixon and Ellis on InAs. Though the exponent would probably be different, the absorption in GaP ought to be similarly affected by changes in concentration of charged impurities. Since the number of charged impurities in GaP should vary with temperature for a reasonably deep impurity level, $\alpha(E_g)$ should likewise vary with temperature. In Fig. 72, $\alpha(E_g)$ decreases proportionally to $1/T$ which is what would be predicted for the contribution of a single donor level. Since the theory of this effect in an indirect transition semiconductor has not been worked out, no further correlations as to energy levels, etc., is possible.

In summary, the agreement between the measured band edge optical absorption of gallium phosphide and that predicted from theory is quite good. The value of the energy gap of $2.312 - 4.2 \times 10^{-4} T$ ev agrees well

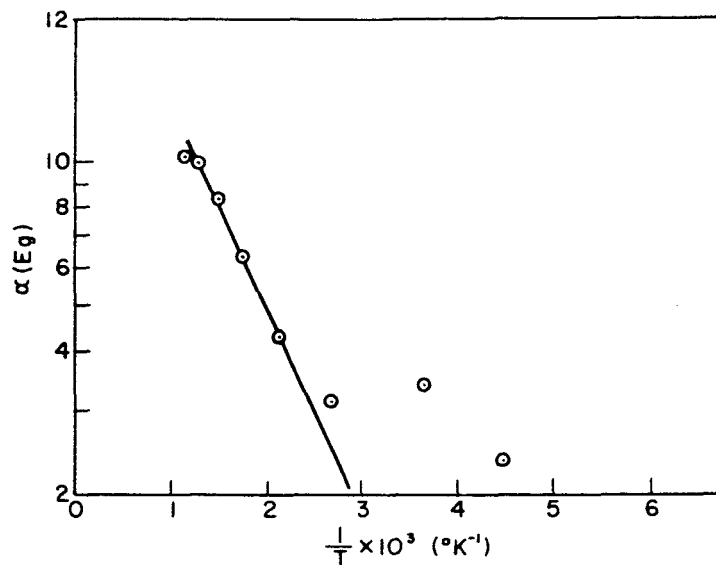[3] D. Redfield, Phys. Rev., 130, 916 (1963).

FIG. 72. $\alpha(E_g)$ VS $1/T$.

with that obtained by other workers [Ref. 4]. The energy for the contributing phonon(s) in the transition of 0.034 ev is reasonable but since neutron diffraction data on the phonon spectrum is not available for GaP it cannot be accurately checked. It is hoped that purer samples of GaP will become available for measurement to determine further the effect of impurities on the observed exponential tail.

PROJECT 5006:   EPITAXIAL GROWTH OF GaP

National Aeronautics and Space Administration
Grant NsG 555
Project Leaders: J. L. Moll and G. L. Pearson
Staff: T. Koike

The purpose of this project is to apply the close-spaced epitaxial growth technique to GaP in order to study its optical and electrical properties.

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[4] M. Gershenzon, D. G. Thomas, and R. E. Dietz, Proc. International Conference Semiconductor Physics, Exeter, 1962, The Institute of Physics and the Physical Society, London, 1962, p. 752.

GaP is transported to a GaAs substrate as described in the previous report. The epitaxial deposition system is shown in Fig. 73. The quartz reaction tube contains two carbon blocks and in between these two carbon blocks the GaP polycrystalline source is separated by 20 to 40 mils from the GaAs substrate. The temperature difference is set by the relative position of the rf coil and the carbon blocks. The amount of water vapor is controlled by passing the hydrogen over ice which is maintained in the salt-ice bath.
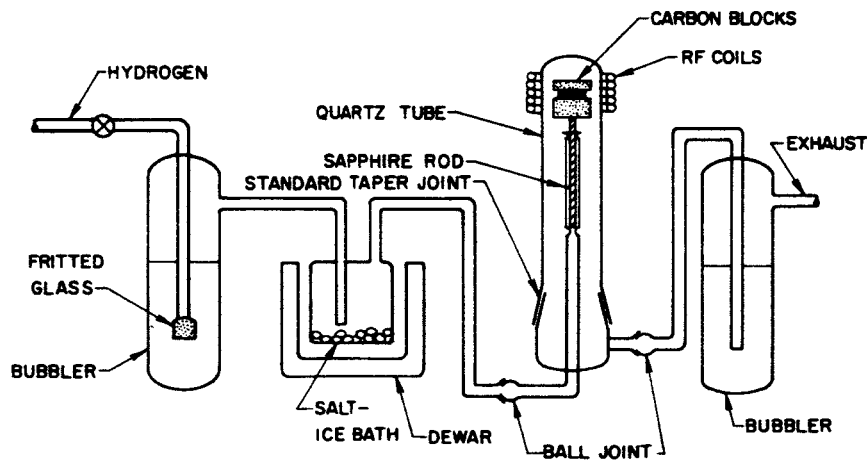
FIG. 73. THE EPITAXIAL GROWTH SYSTEM.

The system has been operated in most cases with considerable success and single crystal epitaxial layers of various thickness have been produced. Some of the grown crystals were tested by the Kossel line technique and were found to be high-quality single crystals. Although we have proved the feasibility of this technique, we have not yet acquired the best operating conditions because of many factors to be taken into consideration. Such factors are:

1. Source temperature

2. Substrate temperature

3. Temperature difference

4. Spacing

5. Flow rate and water content of the hydrogen gas

6. Substrate composition, etc.

Research on the interdependences of these factors is being continued to obtain a reproducible growing technique.

The future work is aimed at establishing this technique and applying it to the epitaxial growth of $GaP_x As_{(1-x)}$.

PROJECT 5108: A STUDY OF $GaAs_xP_{1-x}$ ALLOY

National Aeronautics and Space Administration
Grant NsG 555
Project Leader: G. L. Pearson
Staff: Yen-sun Chen

The objective of this project is to evaluate the optical, electrical and metallurgical properties of the $GaAs_xP_{1-x}$ alloy. Among evaluations of particular interest to us are investigations of the crystal structure

and its imperfections by the Kossel line technique and by that of the
lattice absorption spectra as the mole fraction of GaAs, x, varies
from 0 to 1.

Recent results from measurements of lattice absorption bands in the
spectral region between 10μ and 25μ are presented here. These are from
samples of 75 percent As and 18 percent As, both from Merck Co.*
The carrier concentration in these samples is of the order of 10^{16} –
10^{17} cm^{-3} n-type. The absorption coefficient α of the 75 percent As
sample is plotted against the wave number in cm^{-1} in Fig. 101, while that
of the 18 percent As sample is shown in Fig. 102. For convenience of
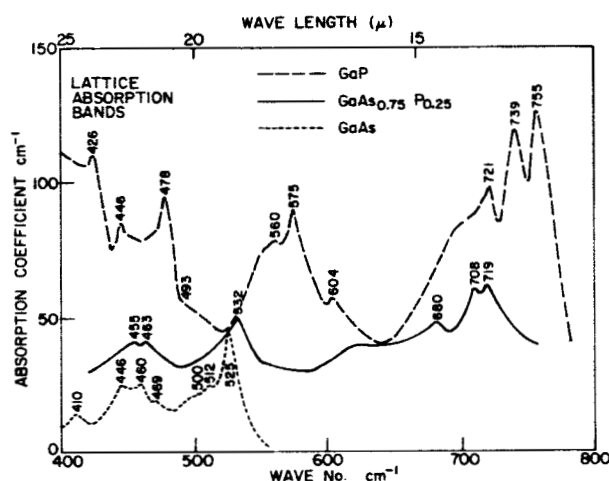
FIG. 101.   LATTICE ABSORPTION BANDS
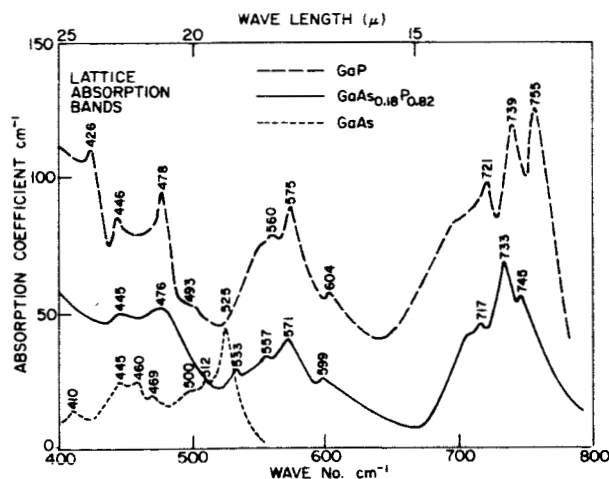OF 75 PERCENT As SAMPLE.

FIG. 102.   LATTICE ABSORPTION BANDS
OF 18 PERCENT As SAMPLE.

*The 18 percent As sample was borrowed from H-P Associates, Palo Alto.

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comparison, we have also plotted in each figure the absorption bands of GaAs and GaP [Ref. 1]. Each peak is described by its measured wave number in cm^{-1}. These samples were also checked for transmission in the visible region to determine the band gap; and by the Kossel line technique to determine lattice constant and defect structure.

The following information is obtained from our data:

1. Generally, the lattice absorption bands of $GaAs_x P_{1-x}$ are a mixture of the bands of GaP and GaAs in the corresponding wave number region. The peaks are shifted, however, those of GaP towards lower wave number and those of GaAs toward higher wave number.

2. In particular, we see the peak at 525 cm^{-1} (100 percent As) has shifted to 532 cm^{-1} (75 percent As) and further to 533 cm^{-1} (18 percent As). There is no doubt that the peak at 533 cm^{-1} is from GaAs since GaP has an exceedingly low absorption in this region.

3. The peaks at 604 cm^{-1} (0 percent As) left out by Kleinman and Spitzer [Ref. 2] in their assignment of combination bands is still present in the GaP rich crystal but shifted slightly to 599 cm^{-1}. Thus we think the 604 cm^{-1} band must be characteristic of GaP rather than due to the molecular vibrations of an unidentified impurity as suggested by Kleinman [Ref. 2].

4. The peaks at 680 cm^{-1}, 708 cm^{-1}, and 719 cm^{-1} (75 percent As) must be from the peaks characteristic of GaP, as again GaAs has an exceedingly low absorption in this region. This result leads us to believe that we will see a gradual shift of all peaks as the value of x varies from 0 to 1 in the mixture. This was not the case, however, in Braunstein's work [Ref. 3] on Ge-Si alloys; there, the combination bands become somewhat smeared in the region $x \cong .50$.

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[1] See SEL QRR No. 8 on the same project.

[2] D. Kleinman and W. Spitzer, "Infrared Lattice Absorption of GaP," Phys. Rev., 118, 110, (1960).

[3] R. Braunstein, "Lattice Vibration Spectra of Ge-Si Alloys," Phys. Rev., 130, 879 (1963).

Earlier work by Braunstein, Moore, and Herman [Ref. 4] showed that
the equivalent temperature of phonons involved in the indirect band gap
electronic transition in Ge-Si alloys varied with composition as shown
in Fig. 103. They tried to interpret the result through short-range
order in the crystal lattice, but were unsuccessful in giving any physical
reason why the S-shaped curve shown in Fig. 103 is followed rather than
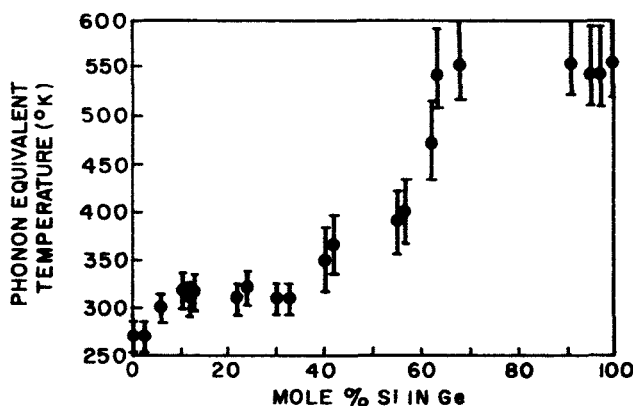any of three other curves which were also derived from their model.

FIG. 103. THE CHARACTERISTIC TEM-
PERATURE OF PHONONS PARTICIPATING
IN THE NONVERTICAL TRANSITIONS IN
Ge-Si ALLOYS AS DETERMINED BY
BRAUNSTEIN, MOORE, AND HERMAN [REF.
4] FROM THE INTRINSIC ABSORPTION
EDGES.

From the data by Braunstein [Ref. 3] on Ge-Si alloy and that pre-
sented here on $GaAs_xP_{1-x}$, it is apparent that the short-range order in
the crystal as proposed in Ref. 4 cannot explain our results, simply
because of the fact that the corresponding modes of the constituents of
the alloy do not merge as shown by the S-shaped curve. In fact, there
was no evidence that the S-shaped curve in Ref. 4 represents a unique
mode or combination of modes of lattice vibration. We are, instead, in

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[4] R. Braunstein, A. Moore and F. Herman, "Intrinsic Optical Absorption in
Ge-Si Alloys," Phys. Rev., 109, 695 (1958).

favor of the assumption that clustering of GaAs and GaP may exist throughout the alloy system and consequently, the vibrational modes are characteristic of pure GaAs and GaP aggregates.

It is known that both GaAs and GaP are somewhat ionic, thus we should be able to detect the reststrahlen band of the mixtures as well as the combination bands. The restrahlen band is due to the creation of long-wavelength optical phonons through interaction with the radiation field. We plan to investigate this point in order to evaluate the effect of alloy composition on the long-wavelength phonons.

In the coming quarter, we shall also investigate the possibility of growing the mixed crystals needed in this project. The most promising method is that reported by Gibbons and Prehn [Ref. 5]. This technique has two advantages: 1) it is a synthetic method so that source-material is no problem, 2) most important of all, crystals grown by this method exhibit exceedingly high purity.

PROJECT 5109:   EPITAXIAL GROWTH OF III-V SEMICONDUCTOR COMPOUNDS

The purpose of this project is to examine and control the crystallographic and electrical properties of III-V compound semiconducting materials grown epitaxially by vapor deposition. Our interests have been concentrated on the compounds GaP and GaAs and on the determination of the chemical reactions involved in the deposition of these compounds from the vapor phase.

In order to obtain more information on the chemical reactions involved in the synthesis of GaP when Ga and PCl_3 are used as starting materials, the system Ga (excess) - Cl_2 has been studied by optical absorption at high temperatures. The absorption spectra show absorption

[5] J. F. Gibbons and P. Prehn, "Epitaxial Vapor Growth of III-V Compounds," TR No. 4711-1, SEL, Oct. 1963.

band systems which are characteristic of GaCl (Fig. 104). The height of
the 3350$\overset{o}{A}$ peak is a measure of the concentration of GaCl. From its varia-
tion with temperature, the equilibrium constant for the reaction

$$GaCl_3(g) + 2Ga(l) \longleftrightarrow 3GaCl(g)$$
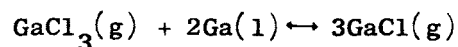
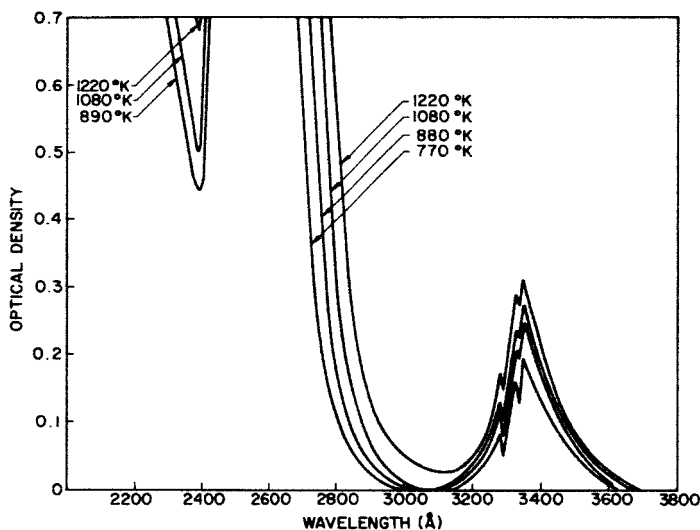has been deduced as a function of temperature (Fig. 105).

FIG. 104. OPTICAL DENSITY OF THE SYSTEM
Ga(excess) - Cl$_2$ VS WAVELENGTH.

Some of the published thermodynamical data for the gallium chlorides
are either uncertain or have been empirically determined. As the equi-
librium constant calculated from these data [Ref. 1] does not fit our
measurements, new values have been deduced for the absolute entropy of
GaCl$_3$ gas and for the enthalpy of GaCl gas.

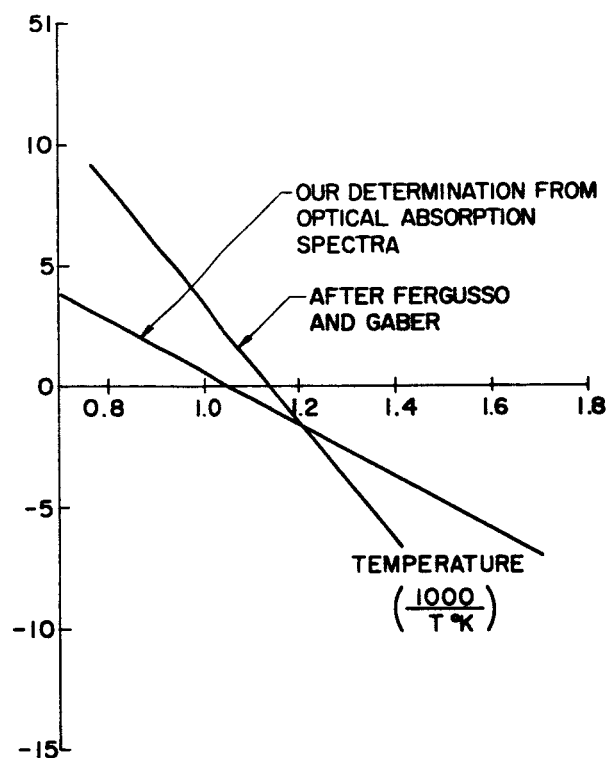[1] R. R. Fergusson and T. Gabor, J. Electrochem. Soc., 111, 585, (1964).

FIG. 105. NATURAL LOGARITHM OF THE
EQUILIBRIUM CONSTANT FOR THE RE-
ACTION $GaCl_3(g) + 2Ga(l) = 3GaCl(g)$
VS RECIPROCAL TEMPERATURE.

Specie	This work	Fergusson & Gabor [Ref. 1]
GaCl(g)	$H^o_f 298$ = -24.7 kcal/mole	-16.2 kcal/mole
GaCl$_3$(g)	$S^o 298$ = 110 e.u.	79.7 e.u.